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Project Title: Niagara River:Assessment and an Innovative AOP Proposal

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested ($): 251,975 **Project Duration:** 2 Years

Abstract:

Complete treatment of recalcitrant organics has been demonstrated in a number of advanced oxidation processes (AOPs) but a significant cost due to competition of radicals, production of toxic intermediates and by-products and system fouling exist. We discuss in this preproposal the use of an AOP that is selective and may hold several advantages over other AOPs currently in use. In this AOP, peroxy-acids are formed when hydrogen peroxide and an organic acid interact with certain types of organic compounds due to significant activity of the peroxy-acid itself or its breakdown product, hydroxyl cation, in an aqueous solution. We have demonstrated that 1-methyl-naphthalene and benzo[a]pyrene disappearance in peroxy-acid treatment is rapid and significant amounts of chemically altered daughter products are formed. The sediment is first contacted with organic acid at a relatively high concentration. This step creates a desorption gradient for hydrophobic contaminants to dissolve and/or desorb from any separate organic or particle associated phases. In the second step, hydrogen peroxide is added to the organic acid solution under controlled pH conditions at a determined dose for a set period of time. The use of this technology for the treatment of sorbed, hydrophobic and particle associated organics offers the potential of significantly increasing solubility of compounds in the organic acid solution thus increasing their susceptibility for subsequent chemical or biological attack.

Geographic Areas Affected by the Project

States:

☐ Illinois
☐ Indiana
☐ Michigan
☐ Minnesota
☒ New York
☐ Pennsylvania
☐ Wisconsin
☐ Ohio

Lakes:

☐ Superior
☐ Huron
☐ Michigan
☐ Erie
☒ Ontario
☐ All Lakes

Geographic Initiatives:

☐ Greater Chicago ☐ NE Ohio ☐ NW Indiana ☐ SE Michigan ☐ Lake St. Clair

Primary Affected Area of Concern: Niagara River, NY

Other Affected Areas of Concern:

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

In 1987, the International Joint Commission's (IJC's) Great Lakes Water Quality Report listed 362 toxic substances that had been positively identified in the lakes, their estuaries, bays, harbors, and rivers. At almost all sites identified as Areas of Concern (AOCs) by the IJC, contamination by toxic substances remains as the major water quality problem. For many of these toxic compounds, the major pathway for (initial) removal from the water column is sorption to suspended particles, followed by bottom deposition. Therefore, contaminated sediments serve as a terminal sink for these particle-associated toxic compounds.

The technology proposed in this research produces in situ a class of soluble oxidants, peroxy-organic acids. This technology has an innovative feature combining both solvent extraction and an advanced oxidation process (AOP). In this technology both sorbed and solution phase with recalcitrant organics will be in contact with strong oxidizing agents (often radicals) under defined conditions of time, temperature, and pH. Although complete destruction of organics is possible in theory, even partial transformation of these recalcitrant compounds will have a significant effect on biodegradability.

The compounds to be examined in this study have been chosen as model compounds that will be used singly (in mechanistic studies) and in combination that present distinct challenges to biodegradation. These compounds include polycyclic aromatic hydrocarbons (PAHs) as target compounds. Other chlorinated organics, particularly chlorinated aromatic compounds like pesticides, octachlorostyrene, and polychlorinated biphenyls (PCBs) will be considered. Many of these compounds may impact receiving environments, displaying acute aqueous toxicity or chronic mutagenic, teratogenic and carcinogenic effects amplified by bioconcentration and bioaccumulation within the food web.

Proposed Work Outcome:

The research approach presented below includes experiments aimed at [1] assessment of the Niagara river sediments, [2] validation of the oxidative method to partially (or completely) degrade hydrophobic and/or recalcitrant organic compounds, [3] optimizing the parameters of the oxidative process, [4] investigating the possible pathways and mechanisms, and [5] determining the effect on biodegradability.

Many hydrophobic organic compounds can be partially degraded using peroxy-acids. Our preliminary studies aimed at contaminated sediment systems has demonstrated that the target compounds, 1-methyl-naphthalene and benzo[a]pyrene, react in the presence of peroxy-acetic acid to produce a suite of metabolites and a number as of yet unidentified daughter products that may be more soluble hydroxylated intermediates. Thus we see this technology having a great promise as a sediment decontamination technology. We will examine here whether the same approach can be used to partially (or completely) destroy target compounds found in Niagara River sediments such as other PAHs, mirex, octachlorostyrene, and PCBs.

Therefore, the overarching objective for the proposed research is to determine the feasibility of a peroxy-acid treatment on contaminated sediment remediation using the following approach: [1] to demonstrate the effectiveness and provide further verification of the peroxy-acid treatment process by testing a variety of recalcitrant organic compounds and using completely-mixed batch conditions, [2] to gain understanding of the reaction mechanism (e.g., the identification of metabolites, measurement of reaction kinetics, and effects of alkalinity, organic macromolecules and other potential scavengers), [3] to optimize the treatment conditions including determination of % by volume composition of acid, choice of organic acid, dose of hydrogen peroxide, and optimal pH, and [4] to assess the usefulness of this AOP as an in-situ and/or ex-situ technique by investigating the impact of this technology to the microbial community structure and the overall chemistry of the sediments in-situ.

The first phase of experiments will be used as a screening tool and will be performed using a detailed study of the selected compounds in DI water. We will examine the "degradation power" by varying the composition of Advanced Oxidation Solution (e.g., organic acid + hydrogen peroxide ratio). In the second phase of experiments the analyses used will be quantitative and qualitative, and kinetic studies will be performed over short time scales. In the third phase, we will attempt to optimize the treatment process by carefully adjusting critical process parameters based on previous results from Phases I and II, but more in detail. Candidate process parameters will include volume percent of the oxidant mixture in the sediment solution, pH, organic acid type, and organic acid:hydrogen peroxide ratio. Several constraints will be considered including the need to minimize the total amounts of organic acid and peroxide used and to minimize reaction time (and hence the volume of oxidant mix needed). Optimization of the pretreatment process will be done using several process assessments as multiple criteria: [1] overall conversion; [2] rate of conversion; and [3] biodegradability of conversion products as multiple criteria. An innovative isotopic method for understanding transformation kinetics and reaction pathways will also be employed in this work. Compound-specific carbon (13C, 12C) and hydrogen (D, H) of residual compounds, reaction intermediates, metabolites and final carbon products (e.g., CO3= , CO2) will be performed in order to assess pathways, product-precursor relationships, and overall carbon mass in the experimental systems and actual sediments. Furthermore, an isotopic calibration of per cent conversion in the experimental system will likely be very useful in assessing reaction progress (e.g., Rayleigh models) in actual field situations.

We propose to conduct additional experiments on sediment collected from the depositional zone in Lake Ontario off the mouth of the Niagara River. Reduction of contaminant levels in both spiked and unspiked samples will be monitored. A sediment core collected in 1995 from a site about 8 km offshore has been radiodated at RPI and found to contain a superb record of continuous deposition from the early 1950s to the mid 1990s. Subsequent analyses provided detailed contaminant chronologies. Core collections during this project will provide the most appropriate sediment for lab experiments. We will also conduct radionuclide and contaminant analyses on samples from the cores to enhance our understanding of the geographic and temporal distribution of contaminants in the extensive depositional area off the mouth of the Niagara River.

Preliminary results on the analysis of spiked sediment samples have demonstrated varied degradation rates depending on the type of acid used and the characteristics of the sediment samples. Within 24 hours, 1-methyl-naphthalene was reduced by 70-100% and benzo[a]pyrene was reduced by 80-100% of its original concentration. Fastest degradation rates were observed in silty-clay sediment samples using acetic acid as the organic acid. This remediation method of PAHs in sediments is fast acting, relatively low-cost, and could be considered as an in-situ technology.

Project Milestones:	**Dates:**
Project Start	09/2000
Calibration of the isotopic method	12/2000
Analytical technique development	06/2001
Organic acid screening	07/2001
Effect of organic acid, H2O2 conc., pH	12/2001
Mass spec product identification	03/2002
Kinetic modeling, process optimization	05/2002
Project End	08/2002

☐ Project Addresses Environmental Justice

If So, Description of How:

☐ Project Addresses Education/Outreach

If So, Description of How:

Project Budget:

	Federal Share Requested ($)	**Applicant's Share ($)**
Personnel:	92,000	27,000
Fringe:	10,600	9,300
Travel:	3,750	1,250
Equipment:	25,000	25,000
Supplies:	30,000	0
Contracts:	10,000	5,000
Construction:	0	0
Other:	1,000	0
Total Direct Costs:	172,350	67,550
Indirect Costs:	79,625	24,420
Total:	251,975	91,970
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Description of Collaboration/Community Based Support:

Dr. J. Kilduff - Environmental and Energy Engineering, RPI
Dr. S. Komisar - Environmental and Energy Engineering, RPI
Dr. R. Bopp - Department of Earth and Environmental Sciences, RPI
Dr. T. Abrajano, Jr. - Department of Earth and Environmental Sciences, RPI